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14. ABSTRACT

This report results from a contract tasking Royal Institute of Technology as follows: The aim of the present proposal is to develop and apply a computer code (DALTON) for studies of multiphoton excitations in charge-transfer materials. The basic technology is density functional response theory, originally developed by the Swedish partner, with the intend of this project to implement in such a way that it becomes practical for large scale, accurate, calculations of charge transfer materials of different size and character. Such materials are very promising for achieving optical control of strong laser light. The final deliverable will include an enhanced version of the DALTON software program that will be available for AFRL/ML to download via a website URL address.

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Modeling of multi-photon excitations in charge-transfer materials

Background

In the last few years one has witnessed an increasing input from theoretical modeling in the design and characterization of materials with properties made-to-order. One branch of such modeling that has developed rapidly concerns the computation of light-matter interaction which now has reached a level of precision to become a practical tool for design of materials with particular optical properties. Vice versa, results on materials properties from spectroscopic and other types of experimental measurements are now commonly analyzed and interpreted by means of computations leading to increased understanding of basic properties and mechanisms, for instance, so-called structure-property and structure-function relationships.

The present project adhered to the general ambition to make quantum computational methods applicable for optical, photonic, properties of technical materials in the non-linear regime. An important non-linear process is two-photon excitation which exhibits some particular features that are of high technological interest, for instance the "control" of strong laser light. Research by many experimental groups have singled out charge-transfer molecules as basic ingredients in useful two-photon materials. The ability to move an electron from one end to another in such a molecule leads to a large change in its dipole moment, something that is directly connected to a large absorption cross section. By absorbing coherently two photons but not a single photon at a time means that the light is absorbed when it is very intensive (the two-photon cross section is quadratically dependent on the intensity), while it still can penetrate the material under normal intensity conditions. Moreover, by reaching fundamental optical excitations by means of infrared light, two-photon absorption shows deeper penetration. These features underly some of the above indicated technological applications of two-photon materials.

However, from the theoretical point of view it has been hard to meet some of the expectations in the field of two-photon technology as fundamental charge transfer excitations are difficult to describe by theoretical modeling unless the molecules are not very small and simple. This owes to the long-range nature of a charge transfer excitation which is not properly invoked in current density functional theory, which is the one most applicable and widely used of the now available electronic structure theories.

Project Plan

The intention with this project was to implement density functional theory in such a way that it became a practical tool for simulations of multi-photon excitations. The goal was to achieve a close to black-box implementation that is useful for a variety of materials and photonics processes, but with particular emphasis on multiphoton excitations in charge transfer materials. On the one hand, a new extension of density functional theory was developed for charge transfer excitations, and a sequence of computational so-called linear scaling algorithms developed, that constitute efficient means for calculations of very large systems. The project goal was to put these things together, so that in a 6-month period the toolbox is ready to go. The project was planned to be carried out in a few steps:

Breakdown of Project Plan:

1) Subproject 1: Finalizing the implementation of the CAM-B3LYP density functional.

2) Subproject 2: Increase speed of two-photon calculations by means of interfacing to the density fitting algorithm.

3) Subproject 3: Increase size of molecules for two-photon simulations by means of interfacing to the linear scaling algorithm.

4) Subproject 4: Porting DALTON program, with the new features, on computers at the Wright-Patterson Air Force Research Laboratory.

5) Subproject 5: Embark on a set of applications on charge-transfer molecular materials.

Result of the project:

The project was successful in all parts:

Subproject 1: Completed. The recently proposed CAM-B3LYP exchange correlation energy functional, based on a partitioning of the r12 operator in the exchange interaction into long- and short-range components, was implemented and assessed for the determination of molecular thermochemistry, structures, and second order response properties. Rydberg and charge transfer excitation energies and static electronic polarisabilities are notably improved over the standard B3LYP functional; classical reaction barriers also improve. Ionization potentials, bond lengths, NMR shielding constants and indirect spinspin coupling constants are comparable with the two functionals. In this projedct we have implemented and evaluated this functionals for two-photon absorption. We have examined the performance of the CAM-B3LYP exchange correlation energy functional for the evaluation of a wide range of molecular properties. The key observation is the improvement in long-range properties such as Rydberg and CT excitation energies, and electronic polarizabilities. This improvement is not associated with any significant increase in computational cost. For several other properties, CAM-B3LYP is comparable to B3LYP. For some properties, most notably atomization energies, CAM-B3LYP cannot compete with B3LYP. Further investigation of Coulomb-attenuated

functionals is now required. CAM-B3LYP is far from optimal and we are confident that further improvements can be made. We highlight three areas that must be addressed. First, we have demonstrated the importance of the so-called a + b = 1 condition; future Coulomb-attenuated functionals must incorporate such a condition in order to further improve long-range excitations. Second, the choice of GGA exchange and correlation functionals is not optimal; the scheme must be applied to newer forms such as Becke's 1997 expansion. The choice of expansion highlights an important observation regarding the gradient corrected exchange in the present study. The discussion leads us to consider an alternative approach, where the Coulomb attenuation is applied to the local density exchange only A gradient corrected exchange term and a correlation functional could then be added, and their parameters optimized.

Subproject 2: A considerable achievement has been obtained in speed and applicable size through this implementation. The actual speedup depends on the size and character of the system, but on average a factor of 5 has been accomplished.

Subproject 3: Implementation successful: We have now been able to carry our TPA calculations on considerably larger systems (in 1, 2 and 3 dimensions). There is still some concern about the stability of wave function / density optimization for larger systems, but these problems are worked on. 200 atom systems are now routine. For the energy, density and wave functions, 3-dimensional 5000 atom systems have been reached. A concomitant development now takes place for properties including TPA. A large span of density functionals are now implemented for these calculations.

Subproject 4: DALTON was right at the start ported on the appropriate computers at the Wright-Patterson Air Force Research Laboratory in Dayton. The most extended versions (not yet publically available) containing Coulomb attenuated algorithms were also ported on these computers, for easy access to Dr. Ruth Pachter and her group.

Subproject 5: Applications have concerned a great variety of molecular systems of charge transfer character. We have addressed these as potential optical power limiting materials by combining first principles quantum mechanical calculations of molecular properties with time-domain solutions of Maxwell equations. We demonstrated this modeling approach on pi-conjugated platinum acetylides that in recent experimental work has been shown good characteristics.
The power limiting capability is explained in terms of a Jablonski diagram; the theoretical simulations include excited state properties both in the singlet and the triplet manifold of states and by combining the molecular property calculations with a light propagation model in order to retrieve estimates of the final property of interest, namely the clamping level of the material. Such a development is expected to have a large impact on the possibility to design molecular materials for OPL applications by theoretical simulations. It is found that knowledge of the intrinsic molecular properties can with advantage be combined with classical pulse propagation in order to address the strong dependence of clamping levels on the laser pulse characteristics, such as intensity, shape and duration time.

As an other example of applications we report the studies of dissolved alkylfluorene-based charge transfer chromophores. These have been extensively studied experimentally in the Air Force Lab in Dayton, and now also theoretically by the computational group at AFRL (Dr. Ruth Pachte et al) partly using the code ported in this project. The purpose of our study was to reveal key processes and properties for the all-over pulse propagation of a realistic system of experimental and theoretical interest. We focussed first on the underlying quantum chemical requirements of having a density functional with proper asymptotic dependence for charge transfer excitations – that is using the here implemented CAMB3LYP functional. With this as basis we studied the conditions for modeling pulse propagation for both short and long pulses. The notion of a strong competition between coherent and incoherent, stepwise, processes, was highlighted in the latter case, meaning that even at resonant conditions stepwise TPA will contribute to the total effective TPA as measured in, e.g., a direct transmission experiment with long pulses. Among a number of conclusions of these studies we highlight three: i) A change from short- to long-pulse excitation is demonstrated to increase the absorptive capacity of the nonlinear medium owing to enhancements of the nonlinear step-wise processes: ii) The two-photon cross section strongly depends on the way in which the dephasing rate decays when the laser frequency is tuned off-resonant with the corresponding molecular transition: iii) The results of the pulse propagation simulations based on electronic structure data obtained with a new Coulomb attenuated functional is shown to be in much better agreement with the experimental results than those based on data received with traditional density functionals.

General comment on results
The AFOSR grant has, apart from the actual research results described above, made it possible to initiate what can be believed to be a very fruitful collaboration between he Wright-Patterson Air Force Research Laboratory and the Royal Institute of Technology, Stockholm, for deriving efficient multi-photon materials and for realizing many of their potential technical applications.

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